

ISOTOPE EFFECTS IN SUPERCRITICAL WATER--KINETIC STUDIES OF COAL LIQUEFACTION

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INTRODUCTION

The chemistry of coal liquefaction is not very well understood, even after more than two decades of research into the kinetics and mechanism of the process. There have been a number of models for conversion proposed, most of them focused on the several liquefaction products, including preasphaltenes, asphaltenes, oils, and gases. A survey of some of the models has been presented (1), and a common feature among them is the multiplicity of paths connecting all of the components.

Kinetic model studies have invariably been carried out in organic donor media, and while the use of these media may be convenient in large scale conversion systems, they do not lend themselves well to laboratory study of conversion. Not the least significant of the problems to be faced in such a study is the unavoidable participation in the overall chemistry of various interrelated and interlocked free radical chain reactions, most of which having no direct bearing on, and perhaps only a secondary relationship with, the liquefaction process.

The complications presented by this network of incidental reactions, coupled with the multiple reaction paths to products, prompted the study of the kinetics of coal liquefaction using supercritical water as the medium. The action of CO/water to reduce both low rank and bituminous coals to upgraded products has been known for more than half a century, having been introduced in the work of Fischer and Schrader (2). Hydrothermal media are recognized as being excellent solvents for aromatics, with tetralin and naphthalene, for example, being fully miscible with water at all proportions at temperatures as low as 300°C (3). A review of the CO/water conversion process, including the most recent work, has recently appeared (4).

In the research described here, batch runs were performed using samples of an Illinois No. 6 coal (PSOC 1098) in a stirred, 300 ml stainless steel autoclave. All of the runs were for 20 min at 400°C. The only product considered is the toluene-soluble fraction (TS), separated from the toluene-insoluble fraction (TI) by simple filtration.

RESULTS

Working Model. Our working model evolved from consideration of the profiles typically noted in the modeling literature. Products are seen to grow with time, and then level off at some level below quantitative conversion. At the same time the quantities "unreacted coal" decline, leveling off at a value above total conversion. A picture of the coal organic matrix derived from this view of conversion would depict a collection of organic units, connected to each other through a series of links increasingly more difficult to break.

On this basis conversion is limited by coal structure. And in terms of the conventional homolytic scission/H-capping view of conversion, increased yields of coal liquids are therefore obtainable only through increases in conversion temperature or residence time. Unfortunately, increases in the thermal severity of the process result in products reflecting the rise of dealkylation and aromatization reactions at higher temperatures. Thus increased product yields are brought about at a considerable cost to product quality (5).

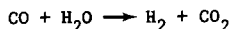
The fact that the profiles of both the desired soluble product and the insoluble product ("unreacted coal") level off at intermediate values suggest a simpler model for conversion. This scheme, presented in Figure 1, is our working model, and is tested in the study described here. In the scheme coal is partitioned in parallel, competitive routes between i) reaction with some reducing component in the system to yield TS, and ii) thermal loss of convertible sites to yield char. In this work we have avoided consideration of specific mechanism for decrease in molecular weight with liquefaction, including in particular the perceived need for thermal scission of C-O and C-C bonds during conversion. Thus we view conversion simply as a process requiring some kind of nonspecific reduction chemistry.

This two-reaction scheme, if truly operative, suggests a view of the potential utility of liquefaction more optimistic than that derived from the conventionally accepted scheme. The yield of TS is a function of the rates of the two reactions. Therefore an increase in the rate of the TS route, or a decrease in the rate of char formation, would bring about increased TS yields. In turn, an increase in the rate of TS formation could be brought about with an increase in the reducing capacity of the system, rather than through an increase in reaction temperature. And thus in principle, increases in TS yield to product quantities representing all of the convertible portion of the starting coal could be obtained, and at no cost to product quality.

CO/Water Conversions. In contrast to the more-or-less fixed reducing capacity available in conventional donor systems, the CO/water system offered considerable latitude. We had earlier demonstrated that changes in the initial pH of the system brought about wide variation in the TS yields for Illinois No. 6 coal (6). In accord with the findings of several other groups including Appell, *et al.* (7), the conversions were found to be base promoted. The present study included a range of initial pH values, and focused on a comparison of the results in H₂O with those from a substitution in parallel experiments of D₂O.

The results for several runs in the two media are presented in Figure 2. The figure presents a plot of %toluene soluble products vs quantity of H₂ produced in the run (cold). There is a range of TS yields from values up to around 50% for the protio medium. These conversions were attained by ranging the initial pH from 7 to 13.

We have pointed out that the water gas shift reaction



parallels the conversion (6), and the results when presented as a function of product H₂ show that the hydrogen from this reaction is not the effective reducing species. Thus in the figure is a result for a run with H₂/H₂O, plotted at an abscissa value equal to the starting quantity of hydrogen (cold). This point falls well below the CO/H₂O results, and it is clear that the TS yield is below that which would be produced for a run with CO yielding that quantity of hydrogen.

Also present in the plot is a result for a conversion in tetralin for 60 min at 400°C. Again the hydrothermal CO system provides the superior results, and at a

shorter residence time.

The major finding in this work is the isotope effect. We find that the deuterio system provides higher TS yields than does the protio system. Moreover, the deuterio results level off at a substantially higher conversion level. This result, an inverse isotope effect, is not very common in isotope effect studies, and has recently been discussed by Keefe and Jencks (8). The implication of these findings as regards conversion mechanism and structure is considerable, and is discussed below.

Products of Conversion. Conversion product analyses are presented in Figure 3. The procedure used here is that developed by Farcasiu (9), with which we have separated the toluene-soluble fractions into subfractions of increasing polarity. The TS fractions for different coals yield different profiles, and yet we find here for the Illinois No. 6 coal that the TS fractions for conversion in water of 29% and 60% are virtually the same. Further, the TS fraction from the tetralin run is also essentially identical in its profile.

This result can be considered along with the molar H/C ratios for both the TS and TI fractions from several runs, shown in Figure 4. We find that within the bounds of the scatter in the data, the ratios are unchanging with conversion. The TI results include those from a run in which N_2 replaced CO.

DISCUSSION

Taken alone, the conversion profile from the protio work is consistent with the view that the conversion of coal is limited by its structure. Thus if the organic portion of coal contained a limited network of breakable links, the scission of which would liberate about 50% of the material to TS product, then runs with increasing conversion capacity would show increased conversion, leveling off at about 50% TS yield.

The inverse isotope effect, however, requires a different picture. Thus a simple change to the heavy medium brings about not only increased conversions, but a leveling off of conversion at a significantly higher level. Whatever the reduction mechanism, it is highly unlikely that isotopic switch from 1H to 2H would increase the inherent bond breaking capacity of the system. And so we conclude that the starting coal must contain many more breakable links than supposed above, but that some portion of the links are lost through other reactions. The proposed model in Figure 1 is thereby confirmed.

The full scheme for conversion is presented in Figure 5. In this scheme, formate is partitioned between reaction with coal, and a hydrogen ion transfer reaction with water to yield formic acid. The acid is unstable at the conversion temperatures (10), decomposing rapidly to carbon dioxide and hydrogen. Thus with the switch from protio to deuterio, the formic acid formation experiences a normal deuterium effect, i.e. protio > deuterio, and is slowed. The result is an increase in the steady-state concentration of formate, and an accordant increase in the TS yield.

These results, including most especially the product data, contrast decidedly with those discussed by Whitehurst *et al.*, noted above (5). In the present work, we find that with increased reducing capacity and at constant temperature, the system gives increased yields of product, and at no cost to product quality.

In summary, we find that conversion is not limited by coal structure, but rather by the kinetics of the reducing step(s). Systems with even greater reducing capacity, and where the water gas shift reaction can be suppressed, should provide even higher conversions to toluene-soluble products. The products in turn should be

no less rich in hydrogen than those from lower conversion runs.

It is still necessary to bring about an understanding of the specific reducing chemistry. From our present data we can conclude that the conventional thermal scission/H-capping sequence does not apply here. And since the TS product from tetralin conversion is no different from those from aqueous conversion, it would appear that the reduction in conventional donors breaks the same links broken by the hydrothermal system.

Thus the question of the nature of critical link scission in conventional conversions must be reconsidered. Brower has recently questioned the conventional scheme (11 a,b), and it is clear that the detailed mechanism of coal conversion is yet to be developed.

NOTE ADDED IN PROOF. The model dealt with here demands that the TI fractions be unconvertible in subsequent conversion attempts. That expectation is realized in work proceeding at present, in which the product from N₂/water runs is being studied. The product, virtually fully toluene-insoluble, yields only 5% TS yields in subsequent CO/water conversions. In fact when the times for the N₂/water runs are reduced to only around 1 min, the subsequent TS yields are still below 10%. The char-forming reaction must be very rapid at 400°C.

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REFERENCES

1. G. Mohan and H. Silla, *Ind. Eng. Chem. Process Des. Dev.*, **20**, 349-358 (1981).
2. F. Fischer and H. Schrader, *Brennst.-Chem.*, **2** 161-172, (1921); *C.A.* **15**, 3193.
3. G. M. Schneider and R. Jockers, *Ber. Bunsenges. Phys. Chem.* **82**, 576-582 (1978).
4. D. S. Ross in "Coal Science," M. Gorbaty, J. Larsen and I. Wender, eds., Academic Press, Inc., New York, 1984, pp. 301-338.
5. M. Farcasiu, T. O. Mitchell and D. D. Whitehurst, *Chem. Tech.* **7**, 680-686, (1977).
6. D. S. Ross, J. E. Blessing, Q. C. Nguyen, and G. P. Hum, *Fuel* **63**, 1206-1210 (1984).
7. H. R. Appell, R.D. Miller and I. Wender, presented before the Division of Fuel Chemistry of the American Chemical Society, 163rd National Meeting of the ACS, April, 1972.
8. J. R. Keeffe and W. P. Jencks, *J. Am. Chem. Soc.*, **103**, 2457-2459 (1981).
9. M. Farcasiu, *Fuel* **56**, 9-14 (1977).
10. V. I. Stenberg, R. L. Van Buren, R. L. Baltisberger, and N. F. Woolsey, *J. Org. Chem.* **47**, 4107-4110 (1982).
11. a) K. R. Brower, *J. Org. Chem.* **47**, 1889-1893 (1982);

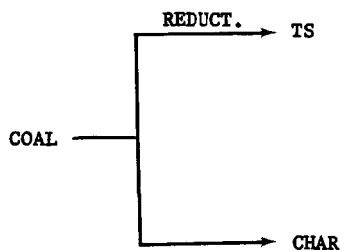


Figure 1. Working Model. TS = toluene soluble

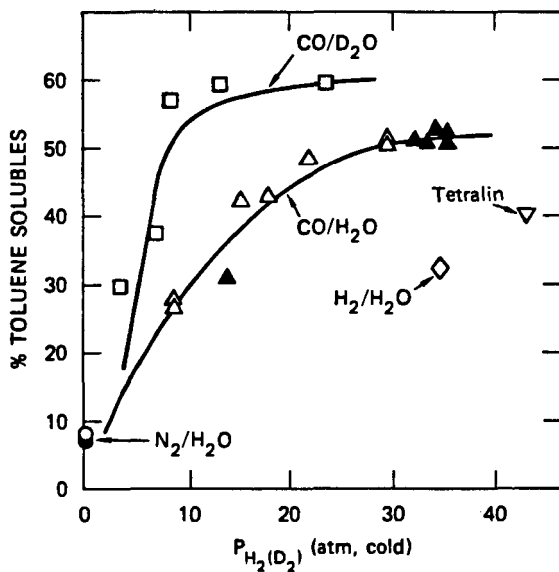


Figure 2. Plot of TS vs Final H₂. The runs were at 400°C for 20 min.

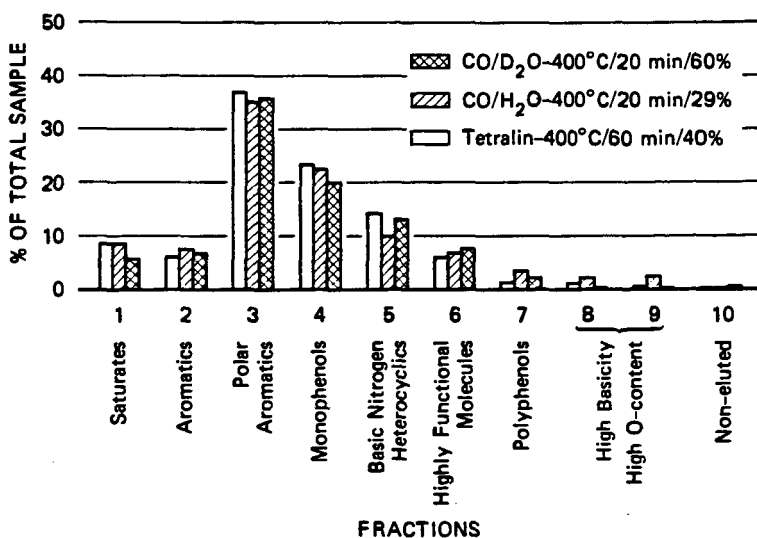


Figure 3. SESC Separations of TS Fractions.

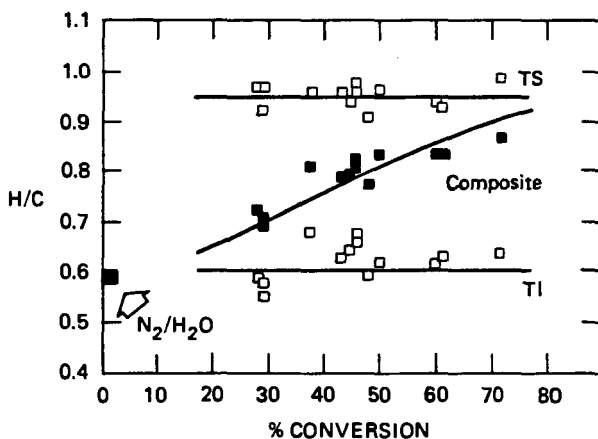


Figure 4. H/C Ratios vs %-Conversion.
The N₂/H₂O point refers to a run in which CO was replaced by N₂.

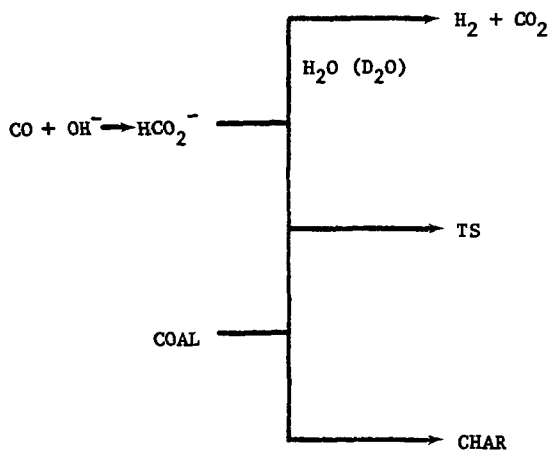


Figure 5. Overall Scheme for Conversion in Hydrothermal Systems